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70 Proprietor: The Clorox Company
1221 Broadway
Oakland California 94612 (US)

71 Inventor: Kaufmann, Edward Joseph
3704 Andalucia Court
San Ramon California 94583 (US)
Inventor: Wiersig, James Ray
1488 Arbor Avenue
Los Altos California 94022 (US)
Inventor: Wilts, James Francis
2910 Maricopa Avenue
Richmond California 94894 (US)

7A Representative: Smith, Sydney et al
Elkington and Fife Beacon House 113 Kingsway
London WC2B 6PP (GB)

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EP 0 158 464 B1

Description

The within disclosed invention relates to detergent mull compositions and delivery means therefor. It is well known to those skilled in the art that nonionic surfactants are useful in formulating laundry
 5 detergents for use in low water temperature washes. It is further known that nonionic surfactants are particularly efficient at removing oily soils from synthetic fabrics but that they are not as efficient at removing particulate soils as anionic surfactants. As a result it is desirable to include detergent builders in detergent formulations containing nonionic surfactants to improve performance on particulate soils and provide good overall cleaning performance. However, the amount of nonionic surfactant that can be
 10 included in powder detergents is limited by the amount that can be absorbed into or adsorbed onto the solid components. Agglomeration techniques usually produce dense particles that have little capacity for absorbing nonionic surfactants and the final compositions usually have poor solubility rates and flowability. Spray-drying techniques produce more porous particles that can sorb more nonionic surfactant. However, the temperatures involved in spray-drying can cause oxidation of the nonionic
 15 surfactant and it is desirable to add the nonionic surfactant in a second step if a high concentration is desired. Since the spray-drying process is energy and capital intensive, this approach results in high manufacturing costs. In addition, if certain builders are present, the spray-drying process itself can lead to the formation of insoluble particles that deposit on clothes during the washing process.

High levels of nonionic surfactants can be readily incorporated into liquid laundry detergents. However, these formulations are normally severely limited in the type and amount of builder that can be incorporated therein since the builder must be soluble or dispersible in the formulation to prevent phase separation. As a result, the overall particulate soil removal performance of liquid laundry detergents is generally poorer than that of powder detergents.

US—A—4316812, issued to Hancock et al, corresponding with DE—A—2825218, appears to disclose
 25 liquid detergent compositions containing builders, a bleach, and nonionic surfactant system, in which the solids have preferably an average particle diameter of less than 10 μm and the nonionic surfactant system has a pour point of less than 10°C. However, it is expensive and inconvenient to use most conventional builders and most other solids at such a small particle size and a potential for the development of health and safety problems related to dusting with these builders and solids exists. Post milling the composition
 30 to reduce the particle size of the solids may eliminate the health and safety problems, but it requires an extra processing step that is energy intensive, and it generates significant heat which may affect temperature-sensitive compounds of the composition. Furthermore, it may have a deleterious effect on encapsulated materials within the composition. Furthermore, no mention is made of the solubility characteristics of these formulations in cold water, and the presence of a dispersing agent like finely
 35 divided silicone dioxide is required.

There have been attempts to combine high levels of nonionic surfactants and builders in laundry detergent formulations which have the physical form of mulls or pastes. US—A—4264466, issued to Carleton et al, describes detergent mulls which contain chain structure clays to prevent phase separation of
 40 the liquid and solid components. US—A—4409146 issued to Cheng, discloses a paste detergent composition containing a specific nonionic surfactant along with a relatively high amount of water.

Because of the viscous nature of these paste formulations, it is difficult to deliver them into the washing machine from a conventional, liquid laundry detergent bottle, even one equipped with a pump dispenser. The use of a squeezable tube, similar to those used to dispense toothpaste, to dispense a liquid
 45 detergent in the form of a paste may be feasible from a technical consideration, but the size of the tube required to contain a reasonable amount of detergent for multiple wash loads would make it difficult for the consumer to use conveniently.

The use of pouches constructed of water soluble films to deliver unit dosages of laundry additives is well documented. However, there has been no demonstration in the prior art of the use of such pouches to
 50 contain and deliver a composition containing a high level of nonionic surfactant. For example, US—A—4115292, issued to Richardson et al, shows compositions with low amounts of very high pour point nonionic surfactants and relatively high amounts of water in water-soluble polyvinyl alcohol pouches.

The steady rise in energy costs has made energy intensive manufacturing processes much less
 55 attractive. This invention seeks to provide detergent mull compositions containing high amounts of nonionic surfactants which are not produced by such energy consumptive processes.

There has been a trend in domestic laundry towards lowered wash temperatures. This invention seeks to provide detergent compositions in the form of mulls which have excellent solubility or dispersability in cool and cold water and which efficiently remove both particulate and oily soils.

This invention can provide detergent compositions in the form of mulls which have excellent rates of
 60 dispersion/dissolution in cool and cold water and which have good phase stability without the addition of clays or other costly phase-stabilizing ingredients and without the requirement of an extremely small average particle size for the solid components of the mulls.

In some aspects this invention seeks to provide a method for conveniently packing, storing and
 65 delivering these detergent compositions to washing machines.

In one aspect of the invention, there is provided a detergent mull composition comprising:

(a) at least one builder, and

(b) a nonionic surfactant system, and wherein the pour point of the system is less than 24°C (75°F) and the average particle size of the solid components of the mull composition exceeds 10 µm; characterised in that the mull composition which does not contain a clay or finely divided silicon dioxide as dispersing agent has a weight amount excess of builder with respect to surfactant. The detergent mull composition comprises advantageously 0.1 to 5.0% by weight of water as a phase stabilizer.

As will be more specifically discussed herein, the novel detergent mull compositions are rapidly soluble/dispersible in cold water and yet surprisingly provide good removal of oily and particulate soils from both natural and synthetic fibres, even though the HLB values of the surfactant systems of these compositions may be lower than is considered optimum for good detergency.

In a further aspect of the invention, there is provided a low-temperature-effective-detergent mull composition comprising:

(a) at least one builder; and

(b) a nonionic surfactant system, and wherein the pour point of the system is less than 24°C (75°F); and the viscosity of the mull composition ranges from 10,000 to 100,000 mPa · s; characterised in that the mull composition which does not contain a clay or finely divided silicon dioxide as a dispersing agent has a weight amount excess of builder with respect to surfactant; and optionally 0.1 to 5.0% by weight water as a phase stabilizer.

The viscosity range of 10,000—100,000 centipoise (mPa · s) specified above is measured at 25°C and at 6.25 revolutions per minute as measured on a Haake Rotoviscometer with an MVII sensor.

More preferably, the compositions of this embodiment have an average viscosity of 20,000—60,000 mPa · s, and most preferably 30,000—50,000 mPa · s under the same rheological test conditions.

The pour point of the mull compositions according to the invention is preferably less than 19°C (65°F) and most preferably less than 5°C (40°F); when water is present in the detergent mull compositions according to the invention in an amount of 0.1 to 5.0% by weight of the composition (unless otherwise specified, all further measures herein are by percent by weight of the composition) phase separation tends to be eliminated. This eliminates the need for the addition of more expensive materials, such as clays, and reduces the phase separation without significantly reducing the cold water solubility of the composition.

In yet another aspect, the invention provides a premeasured, low-temperature-effective delivery system comprising:

a water soluble delivery pouch which contains a low-temperature-effective detergent mull composition according to the invention.

Furthermore, into any of the inventive detergent mull compositions or into the low temperature effective detergent delivery system described above, there may be added further surfactant which do not render detergent solubility/dispersibility unacceptable, fluorescent whitening agents, bleaches, corrosion inhibiting agents (i.e. anti-corrosion agents), anti-redeposition agents, enzymes, dyes, pigments, fabric softeners, fragrances and other adjuncts.

The invention further provides a method of laundering fabrics by contacting the fabrics with the foregoing detergent mull compositions or with water into which the compositions has been dissolved or dispersed, or by contacting the fabric with water to which the low temperature delivery system has been added.

Recent studies have indicated that the average wash temperature of cold water washes in the United States is approximately 18—19°C (65°F) but the temperature range of cold water washes is from 32°C (90°F) to 4—5°C (40°F), and a significant number of wash loads is done in water with a temperature of less than 10°C (50°F). Surprisingly, many mull detergent compositions consisting predominantly of builders and cold water soluble nonionic surfactants will not dissolve/disperse at an adequate rate in cold water washes. It has been further surprisingly discovered that if the pour point of the nonionic surfactant system in these mulls is lower than the water temperature into which the mull is placed, the mull will dissolve/disperse at a rate sufficient to be acceptable for use as a consumer product. It is desirable to formulate these mulls with surfactant systems with pour points of less than 24°C (75°F), more preferably less than 19°C (65°F), and most preferably less than 5°C (40°F) to make them adequately soluble in most cold water washes.

However, generally, as the pour point of the surfactant decreases, so does its hydrophile-lipophile balance (HLB) value, and thus the pour points of the systems disclosed herein approach values much lower than is generally considered optimum for good overall detergency. As disclosed in Schick, *Nonionic Surfactants*, Vol. 2, p. 607 (1962), optimal detergency was thought present at HLB values of around 13—15. HLB values are calculated from the number of ethylene oxide or other solubilizing groups contained in the particular nonionic surfactant. Surprisingly, the compositions disclosed in this invention nonetheless provide good detergency on both particulate and oily type soils even though the HLB values of these surfactant systems are quite low. In fact, some of the systems disclosed in this invention with the lowest HLB values provide the best overall detergency. There is no disclosure or recognition in the prior art that the dispersion/dissolution rates of these forms of detergents in cold water are highly dependent upon the pour points of the nonionic surfactant used in the formulations. Furthermore, no suggestion has been made in the prior art for conveniently delivering viscous detergent compositions containing high levels of nonionic surfactant into the washing machine.

EP 0 158 464 B1

A further potential problem with mulls containing surfactants with low pour points is that the surfactants are too fluid at room temperature, and as a result, have more tendency to separate from the solids in the mulls. This leads to phase separation upon storage of the detergent composition. It has been surprisingly found that the addition of very small amounts of water to the surfactant system will essentially eliminate phase separation in the final detergent mull composition. Water added in the range of 0.1 to 5.0%, based on the weight of the composition, will adequately control phase separation without significantly reducing detergent solubility or dispersibility. Although not wishing to be bound to any one particular theory, applicants speculate that this effect results from flocculation of the solids in the mull which further increases their capacity to adsorb and absorb the surfactant. This is in contrast to the disclosure in US—A—4264466, which teaches the use of chain structure clays to prevent phase separation. These clays are more expensive to use than water and the formation of the chain structure in the mull will most probably reduce the rate of dissolution/dispersion of the resultant detergent composition in cool water.

The amounts of builders and surfactants that can be included in the formulations disclosed herein can vary considerably depending on the nature of the builders, the final desired viscosity and the amount of water added to the surfactant system. In addition, other additives commonly found in detergent compositions can also be included in the formulations described herein. These include but are not limited to further surfactants which do not render detergent dissolution/dispersion rates unacceptable, fluorescent whitening agents, bleaches, corrosion-inhibiting agents, anti-redeposition agents, enzymes, fabric softeners, perfumes, dyes and pigments.

The amount of builder should desirably be in the range of 30 to 90% by weight of the total composition, with the surfactant system comprising 10 to 70% by weight of the composition and the additional optional ingredients comprising 0 to 60% by weight of the composition. The ratio of these ingredients should be further adjusted along with the level of water, which increases the viscosity when added to the formulation, to provide a mull composition with a viscosity preferably in the range of 10,000 to 100,000 centipoise (mPa · s) at 25°C and 6.25 revolutions per minute as measured on a Haake Rotoviscometer with an MVII sensor, and more preferably in the range of 20,000 to 60,000 mPa · s and still more preferably in the range of 30,000 to 50,000 mPa · s.

Thus, the invention disclosed herein provides for mull detergent compositions that can be manufactured economically, will dissolve or disperse at acceptable rates in cool and cold water, have good overall cleaning performance and have controllable phase separation. Suitable, and preferred, materials for the individual constituents of the novel compositions of this invention are described as follows:

Nonionic surfactant system

The surfactants of choice in the nonionic surfactant system have been selected from the nonionic surfactants including linear and branched, primary and secondary ethoxylated alcohols with an average chain length of 6 to 16 carbon atoms and averaging 2 to 10 moles of ethylene oxide per mole of alcohol; linear and branched, primary and secondary ethoxylated, propoxylated alcohols with an average chain length of 6 to 16 carbon atoms and averaging 0 to 10 moles of ethylene oxide and 1 to 10 moles of propylene oxide per mole of alcohol; linear and branched alkylphenoxy (polyethoxy) alcohols, otherwise known as ethoxylated alkyl phenols, with an average chain length of 8 to 16 carbon atoms and averaging 1.5 to 30 moles of ethylene oxide per mole of alcohol; and mixtures thereof.

Particularly preferred examples of these nonionic surfactants are those containing 6 to 10 moles of ethylene oxide per mole of alcohol. While the invention encompasses branched chain nonionic surfactants, it is well known that for commercial purposes linear nonionics are preferred due to their better biodegradability. Exemplary of such surfactants are the Neodol® (trade name of Shell Chemical Company) ethoxylate series. In particular, preferred surfactants include alcohol ethoxylates such as Neodol 91-6, which is a linear ethoxylated alcohol with a predominant chain length of 9 to 11 carbons and average 6 moles of ethylene oxide per mole of alcohol, with a pour point of 7°C (45°F); Neodol 91-8, having the same predominant carbon chain length as Neodol 91-6 averaging 8.4 moles of ethylene oxide per mole of alcohol, with a pour point of 15.5°C (60°F); Neodol 23-6.5, which is a linear ethoxylated alcohol with a predominant chain length of 12 to 13 carbons averaging 6.5 moles of ethylene oxide per mole of alcohol with a pour point of 15.5°C (60°F); Neodol 25-7, which is a linear ethoxylated alcohol with a predominant chain length of 12 to 15 carbons averaging 7.2 moles of ethylene oxide per mole of alcohol, with a pour point of 21°C (70°F); Neodol 25-9, having the same predominant chain length as Neodol 25-7, averaging 9 moles of ethylene oxide per mole of alcohol, with a pour point of 24°C (75°F); and Neodol 45-7, which is a linear ethoxylated alcohol with a predominant chain length of 14 to 15 carbons, averaging 7 moles of ethylene oxide per mole of alcohol, with a pour point of 21°C (70°F). These particular alcohol ethoxylates are characterised by having HLB values ranging from 12.0 to 14.0 and with hydroxyl numbers (measured in milligrams of potassium hydroxide per gram) ranging from 132 to 92.

Other nonionic surfactants may be selected from the Neodol ethoxylate series containing 1—5 moles of ethylene oxide per mole of alcohol. Exemplary of these particular surfactants are Neodol 91-2.5, which is a linear ethoxylated alcohol with a predominant chain length of 9 to 11 carbons, averaging 2.5 moles of ethylene oxide per mole of alcohol, with a pour point of -15°C (5°F), and an HLB value of 8.1; and Neodol

EP 0 158 464 B1

25-3, which is a linear ethoxylated alcohol with a predominant chain length of 12 to 15 carbons, averaging 3 moles of ethylene oxide per mole of alcohol, with a pour point of 4.5°C (40°F), and an HLB value of 7.9.

Yet another particularly preferred surfactant is Surfonic® JL-80X, which is an ethoxylated, propoxylated alcohol with an average chain length of 10 carbon atoms and averaging 9 moles of ethylene oxide and 1.5 moles of propylene oxide per mole of alcohol, with a pour point of -9.5°C (15°F), and an HLB value of 13, available from Texaco Chemical Company.

Suitable alkylphenoxy (polyethoxy) alcohols, otherwise known as ethoxylated alkylphenols, include nonyl- and octylphenoxypoly (ethyleneoxy) alcohols, such as the Igepal series manufactured by GAF Corporation, e.g., Igepal® CO-210, a nonylphenol average 1.5 moles of ethylene oxide per mole of alcohol, and the Triton® series, manufactured by Rohm and Haas Company, e.g. Triton N-57, an ethoxylated nonylphenol averaging 5 moles of ethylene oxide per mole of alcohol.

The mulls of this invention have nonionic surfactant systems with pour points below 24°C (75°F), more preferably below 19°C (65°F), and most preferably below 5°C (40°F). Combinations of these surfactants may be used in the detergent mulls of this invention. Preferred combinations include those which combine a surfactant with a pour point of at least 15.5°C (60°F) with a surfactant with a much lower pour point such that the pour point of the combination is less than 24°C (75°F), more preferably less than 19°C (65°F), and most preferably less than 5°C (40°F). In practice, the pour point of combinations of these surfactants is usually between the pour points of each individual surfactant, but is not necessarily a weighted average of the pour points of each individual surfactant.

The predominant criterion for choosing the surfactants with particular pour points is the temperature of the cold water wash into which the mulls of this invention will be placed. Cold water wash temperatures in the United States vary greatly depending on both location and time of the year. As mentioned above, the average cold water wash has been determined to be 18-19°C (65°F). However, the cold water wash temperatures can actually range from 32°C (90°F) to 4-5°C (40°F). The mulls of this invention are intended to be soluble in such wash temperatures. Therefore, the pour points of the nonionic surfactant systems within the mulls should be at least lower, more preferably 2.7 Celsius degrees (5 Fahrenheit degrees) lower, most preferably 5.5 Celsius degrees (10 Fahrenheit degrees) lower than the temperature of the wash water into which they are placed.

30 Builders

Suitable builders can be selected in this invention from the inorganic builders such as polyphosphates, orthophosphates, metaphosphates, tetraphosphates, tripolyphosphates, phosphates, pyrophosphates, carbonates, bicarbonates, borates, metasilicates, silicates, polysilicates, aluminosilicates (zeolites) and the alkali metal and ammonium salts of any of the foregoing. Further builders can be selected from such organic builders as nitrilotriacetic acid (NTA) polycarboxylates, polyhydroxysulfonates, citrates, succinates, oxydisuccinates, polyacrylic acid, ethylenediaminetetraacetic acid (EDTA) and the alkali metal and ammonium salts of the foregoing. Mixtures of any of the builders can be used. Two particularly preferred builders are sodium carbonate and sodium tripolyphosphate. An additional preferred builder is sodium polysilicate manufactured by PQ Corporation of Valley Forge, Pennsylvania, under the trademark

40 Britesil®.

As previously mentioned, the combination of at least one builder and the nonionic surfactant system should be readily soluble and/or dispersible in the wash water to which it is added. For the purposes of this invention, the concept of dispersibility includes solubility. For purposes of this invention, satisfactory dispersibility is obtained when an observer is unable to visually discern any localized blue residue on fabrics washed with a mull composition containing a blue dye or pigment, or in the washing machine in which these fabrics were washed.

An additional concept which is relevant to the invention is rate of dissolution/dispersion. Over time, many solid particulates will disperse in water. However, to be acceptable for use in this invention, the mulls should dissolve/disperse in the water at 18-19°C (65°F) within at least 25 minutes with gentle agitation, more preferably within 15 minutes, and most preferably within 10 minutes.

The particle size of the builders is not critical if the viscosity of the composition is adjusted to be in the range of 10,000 to 100,000 mPa · s. As a result, the builder used in this composition can thus be generally used as received from the supplier without an extra processing step to mill the particles to a desired size as required in US-A-4316812.

Further, if the viscosity of the composition is maintained in the appropriate range, no dispersant is required to prevent the builders from separating from the balance of the compositions of this invention. Although US-A-4316812 contends no dispersant is needed for its liquid detergent, in fact, all of its examples include finely divided silica ("Aerosil®"), polyethylene glycol, or a combination of the two as dispersants (cf. Column 4, lines 3-7, and Example 5, column 5, line 54, showing use of polyethylene glycol).

The average particle size of the solid components of the mull compositions of this invention is preferably between 10 to 500 µm, more preferably 50 to 250 µm, and most preferably 50 to 175 µm. The average particle size of one of the preferred builders, sodium tripolyphosphate (STPP)—which, in the Examples following, constitutes a major portion of the solids in the mull compositions—was determined by screening and is set forth in Table I:

EP 0 158 464 B1

TABLE I
Average particle size of STPP

	Percent by weight	Avg. Part. size (μm)
5	34	below 75
	22	75—90
10	16	91—100
	19	100—150
15	8	151—400
	0.5	over 400

As noted above, particle size, however, is not critical, but the amounts of builder, surfactants and water must be adjusted to provide satisfactory viscosity. In the invention, the viscosity should be in the range of 10,000 to 100,000 centipoise (mPa · s) at 25°C and at 6.25 revolutions per minute (rpm) as measured with a Haake Rotoviscometer with an MVII sensor, more preferably 20,000 to 60,000 mPa · s.

In order to meet the desirable criteria outlined above, the inventive mull compositions comprise preferably 30 to 90% by weight of at least one builder, 10 to 70% by weight surfactant system, and 0 to 60% by weight adjuncts (as described below); more preferably 40 to 80% by weight of at least one builder, 20 to 60% by weight surfactant system, and 0 to 40% by weight adjuncts; and most preferably 50 to 75% by weight of at least one builder, 25 to 50% by weight surfactant system, and 0 to 25% by weight adjuncts.

Phase stabiliser

Water has been used in Examples 12—14 below as a phase stabiliser and for viscosity control. In fact, in these particular uses, a clay or other thickener is not utilized. While it is not entirely understood why water may act as a thickener in this invention, it is believed that it may cause flocculation of the solids in the compositions of this invention which leads to further adsorption or absorption of the surfactants. The amount of water required to produce the desired viscosity and adequate phase stability appears to show a critical range. This amount ranges from 0.1% to 5%, more preferably 0.4% to 2% by weight of the composition. Furthermore, deionized water is especially preferred for use, although from a commercial standpoint, tap water appears acceptable.

Fluorescent whitening agent

In the invention, fluorescent whitening agents or brighteners, are preferably added to improve whitening of fabrics. Such fluorescent brighteners can be selected from stilbene brighteners, and their derivatives; styrylnaphthalene brighteners and their derivatives; and styrene brighteners and their derivatives. Exemplary of the derivatives used is the preferred brightener Tinopal® 5BM-XC, produced by Ciba-Geigy A.G., Switzerland. Other brighteners include those disclosed in UK patents 1298577, 2076011, 2026054, 2026566, 1393042; and US patents 3951960, 4298290, 3993659, 3980713 and 3627758.

Optional surfactants

Further nonionic, anionic, cationic and amphoteric surfactants may be combined with the detergent mulls of this invention in a manner to impart greater cleaning where desired, with the proviso that such added surfactants do not render detergent solubility or dispersibility unacceptable, especially in cool or cold water up to 24°C (75°F).

For example, anionic surfactants may be added to increase cleaning of particulate soils. Suitable examples of such anionic surfactants include the ammonium, substituted ammonium (e.g., mono- di- and triethanolammonium), alkali metal, and alkaline earth metal salts of C₈—C₂₀ fatty acids and rosin acids, linear and branched alkylbenzenesulfonates, alkyl sulfates, alkyl ether sulfates, alkanesulfonates, olefin sulfonates, hydroxyalkanesulfonates, fatty acid monoglyceride sulfates, alkyl glyceryl ether sulfates, acyl sarcosinates, and acyl N-methyl taurides.

Further, suitable nonionic surfactants include polyoxyethylene carboxylic acid esters, fatty acid glycerol esters, fatty acid and ethoxylated fatty acid alkanolamides, certain block copolymers of propylene oxide and ethylene oxide, and block polymers of propylene oxide and ethylene oxide with propoxylated ethylenediamine. Also included are such semi-polar nonionic surfactants like amine oxides, phosphine oxides, sulfoxides, and their ethoxylated derivatives.

Suitable cationic surfactants include the quaternary ammonium compounds in which typically one of the groups linked to the nitrogen atom is a C₁₂—C₁₈ alkyl group and the other three groups are short-chain alkyl groups which may bear inert substituents such as phenyl groups.

Further, suitable amphoteric and zwitterionic surfactants which contain an anionic water-solubilizing group, a cationic group, and a hydrophobic organic group include aminocarboxylic acids and their salts, iminodicarboxylic acids and their salts, alkylbetaines, alkylamidopropylbetaines, sulfobetaines, alkylimidazolium derivatives, certain quaternary ammonium compounds, certain quaternary phosphonium compounds and certain tertiary sulfonium compounds. Other examples of suitable

zwitterionic surfactants can be found described in US-A-4005029, issued to Jones, at Columns 11-15. Further examples of anionic, nonionic, cationic and amphoteric surfactants which may be suitable for use in this invention are depicted in Kirk-Othmer, *Encyclopedia of Chemical Technology*, Third Edition, Vol. 22, pages 347-387, and *McCutcheon's Detergents and Emulsifiers*, North American Edition, 1983.

Further adjuncts

Further cleaning adjuncts can include enzymes. Particularly preferred are amylases and proteases. Particularly preferred are proteases such as alkaline proteases, also denoted as subtilisins. Suitable examples include Savinase®, Alcalase®, and Esperase®, all from Novo Industri A/S, Denmark, and Maxacal® and Maxatase® from Gist Brocades, N.V., Netherlands.

Bleaches can also be added to the compositions of this invention, preferably peroxygen bleaches such as percarbonate, perborate, and the salts thereof, e.g. sodium perborate monohydrate, and organic and inorganic peroxy compounds, such as peracids, e.g. perlauric acid, and potassium peroxymonosulfate (available from E.I. du Pont de Nemours, Delaware, under the trade mark Oxone®). Additionally, bleach

activators can be incorporated, such as tetraacetythylenediamine (TAED), ketones or aldehydes. Yet other common detergent additives can be included in the formulas of this invention, such as dyes, pigments and colorants, exemplary of which are ultramarine blue (UMB) pigments, anthraquinone dyes, and Monastral® dyes, which are manufactured by E. I. du Pont de Nemours, Delaware. Especially preferred is UMB to impart a pleasing color to the mull composition as well as to deliver a bluing effect on fabrics. Fabric softeners may be added to the inventive mulls. These fabric softeners are generally quaternary ammonium compounds and their salts, as disclosed in US-A-4250043, issued to Jones, and US-A-4339335, issued to Wixon. Use of such fabric softeners is particularly favoured in the mulls of this invention due to the general absence of anionic surfactants in the mulls' formulations. Further, fragrances of various sorts, most of which are ketones or aldehydes containing substituted phenyl rings, can be added to the mulls. Also, corrosion-inhibition agents and anti-redeposition agents may be included in these mulls.

Delivery films

As noted in the foregoing, because of the physical nature of the mull detergent compositions, packaging and delivery of these compositions into the wash water cannot be implemented efficiently by most current commercial detergent packaging systems. As a result preferred forms of this invention comprise a delivery system comprising (a) a water-soluble delivery pouch, which comprises a film prepared from at least one film-forming polymer and (b) an effective amount of a low temperature detergent mull as described hereinbefore, which comprises a nonionic surfactant system and a builder.

Particularly preferred films are castable, water-soluble films comprised of polyvinyl alcohols which have number average molecular weights from 5,000 to 250,000. The polyvinyl alcohols generally have 1 to 25% residual acetate groups, more preferably 5 to 20% residual acetate groups, and most preferably 10 to 15% residual acetate groups. Additionally, such polymers as polyvinyl pyrrolidone, methyl cellulose, polyethylene oxide, gelatin and other film formers can be utilized. Plasticizers such as trimethylolpropane, glycerol, polyethylene glycol and others known to those skilled in the art can be included in the film to provide the film strength and flexibility required for producing, filling, shipping and storing the pouches prepared from these films. In addition other ingredients such as wetting agents, defoamers, and anti-blocking agents can be included in these films to aid in their manufacture and in the preparation of pouches made from these films.

The films employed can have a thickness of from 25 to 127 μm with the thickness and film material being selected to provide the optimum balance of film strength and cold water solubility. It has been found that films with a thickness of 38 to 89 μm produced from polyvinyl alcohol with about 12% residual acetate groups are preferred.

It has been further found that when pouches are produced from these preferred films and stored in contact with the detergent mulls of this invention, significant losses of impact strength can occur. It has been found however, that the incorporation of small amounts of known film plasticizers into the detergent mull composition itself surprisingly minimizes this loss of impact strength of the films after storage in contact with the detergent compositions. Thus, a further embodiment of this invention comprises a delivery system comprising (a) a water-soluble delivery pouch, and (b) an effective amount of a low-temperature-effective detergent mull as described hereinbefore, which comprises a builder and a nonionic surfactant system and additionally 30% or less, based on the weight of the surfactant system, of at least one ingredient that is suitable for use as a film plasticizer for the film used to form the water-soluble pouch.

This invention is further exemplified by the examples set forth below which are intended to illustrate but not restrict the scope of the invention.

EP 0 158 464 B1

The following detergent formula was used to prepare the mull detergent compositions in Examples 1—10:

Examples 1—10

Ingredient	% by weight
Nonionic surfactant ¹	30.0
Sodium tripolyphosphate ²	55.4
Sodium carbonate ²	10.5
Britesil® C-24 ³	1.5
Alcalase® 2.0T ⁴	0.7
Savinase® 8.0S ⁴	0.7
Tinopal® 5BM-XC ⁵	0.9
UMB Pigment ⁶	0.1
Fragrance	0.2

¹. Disclosed in Table II, below

². Builders.

³. Polysilicate builder with an SiO₂/Na₂O ratio of 2.4:1, manufactured by PQ Corporation of Valley Forge, Pennsylvania.

⁴. Proteolytic enzymes, manufactured by Novo Industri A/S, Denmark.

⁵. Fluorescent whitening agent, manufactured by Ciba Geigy A.G., Switzerland.

⁶. Ultramarine Blue.

Approximately 2 kilograms of each of the 10 exemplified compositions in Table II were prepared by premixing the nonionic surfactants together and then mixing the surfactant system together with the remainder of the ingredients in a Hobart mixer. Relatively low shear mixing was used and a total mixing time of 15—30 minutes was sufficient to provide uniform distribution of the ingredients in the resulting mulls. The pour point of each surfactant mixture was measured using the basic procedure found in ASTM D97-66.

After each composition was prepared, approximately 30 grams of each were placed in individual pouches prepared from Quiksol® A film supplied by Polymer Films Inc. of Rockville, Connecticut, USA. The films were 38 µm thick and were composed of polyvinyl alcohol with an average molecular weight of about 96,000 and approximately 12% residual acetate groups. The mulls were enclosed in the films, which were heat sealed.

The resulting pouches were then placed at 4.5°C (40°F) for 24—48 hours (to simulate storage by the consumer, such as in a garage), removed and their solubility in 4.5°C (40°F) water was evaluated. This procedure involved placing the pouches in a washing machine containing 68 litres of water at 4.5°C (40°F) and initiating a wash cycle using the "delicate" setting to control agitation. After ten minutes, the agitation was terminated, and the machine was drained and inspected for residual detergent. Residual detergent is determined by whether any residue remains which is visually discernible in the washing machine. This is a measure of the dissolution/dispersion rates of the mull compositions. The results are shown in Table II below.

TABLE II

Example	Surfactant system					Pour point	Time for detergent to dissolve at 4.5°C (40°F)
	Neodol ¹ 23-8.5	Neodol ² 25-9	Neodol ³ 25-3	Neodol ⁴ 91-6	Neodol ⁵ 91-2.5	Surfonic ⁶ JL-80X	
1	50%	50%				18.3°C (65°F) ⁷	>10 min.
2			100%			4.5°C (40°F) ⁸	>10 min.
3				100%		7.2°C (45°F) ⁸	>10 min.
4					100%	-15°C (5°F) ⁸	<10 min.
5	50%			50%		11.1°C (52°F) ⁷	>10 min.
6				50%	50%	2.2°C (36°F) ⁷	<10 min.
7	50%				50%	8.3°C (47°F) ⁷	>10 min.
8	50%		50%			10.6°C (51°F) ⁷	>10 min.
9	12.5%					-3.9°C (25°F) ⁷	<10 min.
10	12.5%				18.8%	-4.5°C (24°F) ⁷	<10 min.

1. Ethoxylated linear alcohols (Shell Chemical Company) with a predominant chain length of 12—13 carbons and averaging 6.5 moles of ethylene oxide per mole of alcohol.

2. Ethoxylated linear alcohols (Shell Chemical Company) with a predominant chain length of 12—15 carbons and averaging 9 moles of ethylene oxide per mole of alcohol.

3. Ethoxylated linear alcohols (Shell Chemical Company) with a predominant chain length of 12—15 carbons and averaging 3 moles of ethylene oxide per mole of alcohol.

4. Ethoxylated linear alcohols (Shell Chemical Company) with a predominant chain length of 9—11 carbons and averaging 6 moles of ethylene oxide per mole of alcohol.

5. Ethoxylated linear alcohols (Shell Chemical Company) with a predominant chain length of 9—11 carbons and averaging 2.5 moles of ethylene oxide per mole of alcohol.

6. Ethoxylated, propoxylated linear alcohols (Texaco Chemical Company) with a predominant chain length of 10 carbons, and averaging 9 moles of ethylene oxide and 1.5 moles of propylene oxide per mole of alcohol.

7. Pour point value determined by procedure adopted from ASTM D97-68.

8. Pour point value shown in manufacturer's literature.

EP 0 158 464 B1

Reviewing Table II, one can see that the composition of Example 1, which contains two surfactants, Neodol 23-6.5 and Neodol 25-9, which are considered to be water soluble by their manufacturer, failed to completely dissolve at 4.5°C (40°F) under the test conditions. In addition when this composition was stored at 21°C (70°F) and added to wash water at 17°C (63°F), it again failed to completely dissolve under the test conditions described previously. Example 4, by comparison, which contains Neodol 91-2.5, dissolved/dispersed completely in the cold, i.e. 4.5°C (40°F) water even after storage at 4.5°C (40°F). This was particularly surprising since this particular surfactant is considered by its manufacturer to be less soluble in water than both of the surfactants used in Example 1. Thus, surprisingly, adding a surfactant system that is apparently less soluble in water to the remaining components of Examples 1—10 improved the dissolution/dispersion rates of the mull compositions in cold water.

Further examination of Table II shows that Examples 4, 6, 9 and 10, with surfactant systems with pour points less than or equal to 2.2°C (36°F) completely dissolved/dispersed in 4.5°C (40°F) water under the test conditions described above. Thus, the applicants have concluded that the dissolution/dispersion rates of the mulls of this invention are related to the pour points of the surfactant systems in these mulls and that the pour points should be at least lower than the temperature of the water in which the mulls are placed to provide acceptable dissolution/dispersion rates in the water. Apparently, the examples which have the lower pour point surfactant systems maintain more fluidity in cold water, which facilitates their dispersion. It is surprising that these differences in fluidity of already viscous samples are more important than overall water solubility in controlling the rates of dissolution/dispersion of these compositions in cold water.

Performance studies on cotton, cotton/polyester blends, and polyester fabrics soiled with a synthetic sebum or a synthetic clay soil (Performance Test I) show that reducing the pour point of the surfactant system does not reduce the cleaning efficacy of these compositions even if the HLB value is reduced to a level much lower than that normally prescribed for good detergency. Thus, the compositions of this invention provide good cleaning as well as good solubility/dispersibility characteristics. The cleaning performance was evaluated by washing swatches treated with these soils in water at 38°C (100°F) containing 100 ppm water hardness (as CaCO₃) with a molar ratio of Ca²⁺:Mg²⁺ of 3:1 and a concentration of 0.08% of the appropriate detergent mull composition in a commercial washing machine. The reflectance values of the swatches were measured before and after washing, and the Kubelka-Munk equation was used to calculate % soil removal.

Performance test I

		% Soil removal						
		Cotton		Polycotton		Polyester		
Example	HLB	Sebum	Clay	Sebum	Clay	Sebum	Clay	
1	12.6	87.4	86.7	79.9	99.5	82.1	99.2	
6	10.3	89.1	89.5	80.6	99.6	85.6	99.5	
9	12.9	88.6	89.1	73.1	99.0	81.5	99.4	
10	11.9	89.6	90.2	78.2	100	86.7	100	
LSD ¹		2.6	3.1	4.1	1.5	2.9	0.5	

¹LSD is at 90% confidence level.

It was particularly surprising that Examples 6 and 10 performed so well, since they each contain a significant amount of Neodol 91-2.5, which is not merely considered insoluble by its manufacturer, but unsuitable for good detergency as well. Further surprising results were obtained with Example 10. Example 10 is a ternary system containing mixture of three nonionic surfactants, two of which have very low pour points (Neodol 91-2.5 and Surfonic JL-80X). On two fabrics, cotton and polyester, this ternary system had significantly better particulate (clay) soil removal, than the composition of Example 1, which was unexpected based on the HLB's of the surfactant systems.

Performance test II

Selected examples based on the compositions of Table II were tested for performance at 4.5°C (40°F), under the same conditions as the foregoing, except for temperature and the use of only cotton and polyester fabrics. The results for % soil removal of both sebum (oily) and clay (particulate) soils are shown below:

EP 0 158 464 B1

	Surfactant	HLB	Fabric	% Soil removal ⁴	
				Sebum	Clay
5	Neodol 23-6.5 ¹	12.0	Cotton	75.2	83.9
	Neodol 91-2.5/91-6 ²	10.3	Cotton	82.1	83.2
10	Neodol 23-6.5 ¹	12.0	Polyester	84.1	96.8
	Neodol 91-2.5/91-6 ²	10.3	Polyester	90.7	96.4
	LSD ³			3.9	2.3

1. 100% of this surfactant was used.

2. 50%/50% mixture of these surfactants was used.

3. LSD is at 90% confidence level.

4. Mulls were predissolved in the water before tests were initiated.

The above results show that a combination of nonionic surfactants having a reduced pour point and reduced HLB values surprisingly demonstrated soil removal properties in a low temperature wash as good as or better than a single nonionic surfactant which one would expect to have better solubility and detergency than the combination.

Examples 11—12

50 kilogram quantities of mull detergent compositions were prepared using a ribbon blender and the formulas are summarized below. In Example 12, the water was added to the surfactant system before this system was mixed with the rest of the composition.

	Example 11	Example 12
	%	%
35	Neodol 23-6.5	3.7
	Surfonic JL-80X	26.3
	Deionized water	—
40	Sodium tripolyphosphate	55.4
	Sodium carbonate	10.5
45	Britesil® C-24	1.5
	Alcalase® 2.0T	0.8
	Savinase® 8.0S	0.6
50	Tinopal® 5BM-XC	0.9
	Pigment	0.1
55	Fragrance	0.2

The composition of Example 11 was observed to have phase separation after storage at room temperature. The separation was quantified by placing 1000 grams of the composition in a one-litre graduated cylinder for one week at room temperature and then removing and weighing the separated liquid phase that appeared on top of the remainder of the composition. It was found that weight of the liquid totaled 4.8% of the total composition. When the detergent of composition 12 was evaluated under the same conditions, 0.1% or less liquid phase separation was observed.

Furthermore, 2 kilogram quantities of the detergent composition of Example 12 were prepared and tested for solubility as were Examples 1—10. The composition of Example 12 dissolved/dispersed completely in less than ten minutes in 4.5°C (40°F) water.

EP 0 158 464 B1

Examples 13—14

2 kilogram quantities of mull detergent compositions were prepared using a Hobart mixer and their formulas are summarized below. Approximately 25 grams of each composition were placed in a 2x3 inch (5.08x7.62 cms) water-soluble pouch constructed from a 63 μ m thick film comprised predominantly of polyvinyl alcohol (number average molecular weight of about 10,000 and about 12% residual acetate groups) with 5% glycerol and 4% trimethylolpropane as plasticizers. The pouches were stored for nine weeks at 21°C/50% relative humidity (70°F/50%).

	Example 13	Example 14	
10	%	%	
	Neodol 23-6.5	3.7	3.6
	Surfonic JL-80X	26.1	25.6
15	Deionized water	0.6	0.6
	Sodium tripolyphosphate	55.0	54.0
20	Sodium carbonate	10.5	10.3
	Britesil® C-24	1.5	1.5
	Alcalase® 2.0T	0.8	0.8
25	Savinase® 8.0S	0.6	0.6
	Tinopal® 5BM-XC	0.9	0.9
30	Pigment	0.1	0.1
	Fragrance	0.2	0.2
	Glycerol	—	0.9
35	Trimethylolpropane	—	0.9

After nine weeks of storage, the film from the pouches containing the composition of Example 13 was obviously brittle while the film from the pouches containing the composition of Example 14 was much more flexible. Impact strength measurements made on these films using a Rheos Total Energy Impact Strength Tester and testing conditions of 1.7°C/42% relative humidity (35°F/42%) indicate that the films used with the composition in Example 14 had about five times more impact strength than the films used with the composition in Example 13. As previously discussed, this shows that the addition of the plasticizer directly to the mull minimises the loss of film impact strength when the film is exposed to the mull. This was unexpected and further shows the unobvious characteristics of the delivery system of this invention.

Claims

1. A detergent mull composition comprising:
 - (a) at least one builder; and
 - (b) a nonionic surfactant system, and wherein the pour point of the system is less than 24°C (75°F); and the average particle size of the solid components of the mull composition exceeds 10 μ m; characterised in that the mull composition which does not contain a clay or finely divided silicon dioxide as a dispersing agent has a weight amount excess of builder with respect to surfactant.
2. A low-temperature-effective detergent mull composition comprising:
 - (a) at least one builder; and
 - (b) a nonionic surfactant system, and wherein the pour point of the system is less than 24°C (75°F) and the viscosity of the mull composition ranges from 10,000 to 100,000 mPa · s; characterised in that the mull composition which does not contain a clay or finely divided silicon dioxide as a dispersing agent has a weight amount excess of builder with respect to surfactant.
3. A composition as claimed in Claim 1 or Claim 2 characterised in that it contains 0.1 to 5.0% by weight of water as a phase stabilizer.
4. A mull composition as claimed in any one of Claims 1 to 3 characterised in that at least one builder
 - (a) is selected from: polyphosphates, orthophosphates, metaphosphates, tripolyphosphates, phosphates, pyrophosphates,

carbonates, bicarbonates, borates, silicates, polysilicates, aluminosilicates, metasilicates, and the alkali metal and ammonium salts of any of the foregoing; nitrilotriacetic acid, polycarboxylates, polyhydroxy sulfonates, citrates, succinates, oxydisuccinates, polyacrylic acid, ethylenediaminetetraacetic acid, and the alkali metal and ammonium salts of any of the foregoing; and mixtures thereof.

- 5 5. A mull composition as claimed in any of Claims 1 to 4 characterised in that the nonionic surfactant system comprises at least one nonionic surfactant selected from:
linear and branched, primary and secondary ethoxylated alcohols with an average chain length of 6 to 16 carbon atoms and averaging 2 to 10 moles of ethylene oxide per mole of alcohol; linear and branched, primary and secondary ethoxylated, propoxylated alcohols with an average chain length of 6 to 16 carbon atoms and averaging 0 to 10 moles of ethylene oxide and 1 to 10 moles of propylene oxide per mole of alcohol; linear and branched alkylphenoxy (polyethoxy) alcohols with an average chain length of 8 to 16 carbon atoms and averaging 1.5 to 30 moles of ethylene oxide per mole of alcohol; and mixtures thereof.
6. A mull composition as claimed in any one of the preceding claims characterised in that it further comprises at least one adjunct selected from:
15 an additional nonionic, anionic, cationic, and amphoteric surfactants; phase stabilisers; fluorescent whitening agents; anti-redeposition agents; corrosion-inhibiting agents; bleaches, dyes; pigments; enzymes, fabric softeners; and fragrances.
7. A mull composition as claimed in Claim 6 characterised in that it includes a fluorescent whitening agent which is at least one of stilbene, styrylnaphthalene and styrene brighteners and their derivatives; and/or including a said pigment which is ultramarine blue; and/or including at least one enzyme, which enzymes include amylases and proteases.
8. A mull composition as claimed in Claim 6 or Claim 7 characterised in that the builder (a) is 30% to 90% by weight, the surfactant system (b) is 10% to 70% by weight, and the adjunct (c) is 0% to 60% by weight, of the mull composition.
- 25 9. A mull composition as claimed in Claim 6 or Claim 7 characterised in that it comprises from 50 to 75% by weight of at least one builder, from 25 to 50% by weight surfactant system and 0 to 25% by weight adjuncts.
10. A mull composition as claimed in Claim 8 or Claim 9 characterised in that the pour point of the surfactant system is less than 19°C (65°F).
- 30 11. A mull composition as claimed in Claim 8 or Claim 9 characterised in that the pour point of the surfactant system is less than 5°C (40°F).
12. A mull composition as claimed in any of Claims 8 to 11 characterised in that the surfactant system comprises at least two nonionic surfactants, one of which has a pour point of less than 5°C (40°F).
13. A mull composition as claimed in any of Claims 8 to 11 characterised in that the surfactant system comprises three nonionic surfactants, two of which have pour point of less than 5°C (40°F).
- 35 14. A mull composition as claimed in Claim 8 characterised in that the pour point of the system is less than 19°C (65°F) and the average particle size of the solid components of the mull composition is 50 to 250 µm.
15. A premeasured, low-temperature-effective delivery system comprising:
40 a water-soluble delivery pouch, which encloses a low-temperature-effective detergent mull composition according to any one of the preceding claims.
16. The delivery system of Claim 15 wherein the delivery pouch comprises a film which is prepared from at least one castable film-forming polymer selected from:
polyvinyl alcohol, polyvinyl pyrrolidone, methyl cellulose, polyethylene oxide, gelatin and mixtures thereof.
- 45 17. The delivery system of Claim 16 wherein the polymer is a polyvinyl alcohol with a number average molecular weight of 5,000 to 250,000 and 1—25% residual acetate groups.
18. The delivery system of any one of Claims 15 to 17 wherein the film contains at least one plasticiser.
19. The delivery system of any one of Claims 15 to 18 wherein the mull further comprises (d) at least one film plasticiser in an amount of no more than 30% by weight of the surfactant system.
- 50 20. A method for laundering fabrics comprising:
contacting the fabrics with a detergent mull composition according to any one of Claims 1 to 14 or with wash water into which the composition has been dissolved or dispersed or into which has been dispersed a premeasured, low-temperature-effective delivery system according to any one of Claims 15 to 19.

Patentansprüche

1. Detergens-Mullzusammensetzung, enthaltend:
(a) mindestens ein Aufbaumittel; und
(b) ein nichtionogenes oberflächenaktives System, wobei der Stockpunkt des Systems weniger als 24°C (75°F) ist und die mittlere Teilchengröße der festen Komponenten der Mullzusammensetzung über 10 µm hinausgeht, dadurch gekennzeichnet, daß die Mullzusammensetzung, die keinen Ton oder feinzerteiltes Siliciumdioxid als Dispergierungsmittel enthält, einen als Gewichtsmenge ausgedrückten Überschuß an Aufbaumittel gegenüber dem oberflächenaktiven Mittel enthält.
2. Bei niedriger Temperatur wirksame Detergens-Mullzusammensetzung, enthaltend:

- (a) mindestens ein Aufbaumittel; und
 (b) ein nichtionogenes oberflächenaktives System, wobei der Stockpunkt des Systems weniger als 24°C (75°F) ist und die Viskosität der Mullzusammensetzung im Bereich von 10.000 bis 100.000 mPa · s liegt, dadurch gekennzeichnet, daß die Mullzusammensetzung, die keinen Ton oder feinzerteiltes Siliciumdioxid als Dispergierungsmittel enthält, einen als Gewichtsmenge ausgedrückten Überschuß an Aufbaumittel gegenüber dem oberflächenaktiven Mittel enthält.
3. Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß sie 0,1 bis 5,0 Gew.-% Wasser als Phasenstabilisator enthält.
4. Mullzusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß mindestens ein Aufbaumittel (a) aus:
 Polyphosphaten, Orthophosphaten, Metaphosphaten, Triphosphaten, Phosphaten, Pyrophosphaten, Carbonaten, Bicarbonaten, Boraten, Silicaten, Polysilicaten, Aluminosilicaten, Metasilicaten und den Alkalimetall- und Ammoniumsalzen der vorstehenden Substanzen; Nitrolotriessigsäure, Polycarboxylaten, Polyhydroxysulfonaten, Citraten, Succinaten, Oxydisuccinaten, Polyacrylsäure, Ethylendiamintetraessigsäure und den Alkalimetall- und Ammoniumsalzen der genannten Substanzen; und Gemischen davon, ausgewählt ist.
5. Mullzusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das nichtionogene oberflächenaktive System mindestens ein nichtionogenes oberflächenaktives Mittel, ausgewählt aus:
 linearen und verzweigten, primären und sekundären ethoxylierten Alkoholen mit einer mittleren Kettenlänge von 6 bis 16 Kohlenstoffatomen und im Mittel 2 bis 10 mol Ethylenoxid pro mol Alkohol; linearen und verzweigten, primären und sekundären ethoxylierten propoxylierten Alkoholen mit einer mittleren Kettenlänge von 6 bis 16 Kohlenstoffatomen und im Mittel 0 bis 10 mol Ethylenoxid und 1 bis 10 mol Propylenoxid pro mol Alkohol; linearen und verzweigten Alkylphenoxy-(Polyethoxy)alkoholen mit einer mittleren Kettenlänge von 8 bis 16 Kohlenstoffatomen und im Mittel 1,5 bis 30 mol Ethylenoxid pro mol Alkohol; und Gemischen davon, enthält.
6. Mullzusammensetzung nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß sie weiterhin mindestens ein Hilfsmittel, ausgewählt aus:
 einem weiteren nichtionogenen, anionischen, kationischen und amphoteren oberflächenaktiven Mittel; Phasenstabilisatoren; Fluoreszenz-Weißmachern; Antiwiederabscheidungsmitteln; korrosionsinhibierenden Mitteln; Bleichmitteln; Farbstoffen; Pigmenten; Enzymen; Gewebeweichmachern; und Aromatisierungsmitteln, enthält.
7. Mullzusammensetzung nach Anspruch 6, dadurch gekennzeichnet, daß sie einen Fluoreszenz-Weißmacher, der mindestens ein Stilben- Styrylnaphthalin- und Styrol-Weißmacher und ihre Derivate ist, enthält und/oder ein genanntes Pigment einschließt, das Ultramarinblau ist, und/oder mindestens ein Enzym, welche Enzyme Amylasen und Proteasen einschließen, einschließt.
8. Mullzusammensetzung nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß der Anteil des Aufbaumittels (a) 30 bis 90 Gew.-% beträgt, daß der Anteil des oberflächenaktiven Systems (b) 10 bis 70 Gew.-% beträgt und daß der Anteil Hilfsmittels (c) 0 bis 60 Gew.-% der Mullzusammensetzung beträgt.
9. Mullzusammensetzung nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß sie 50 bis 75 Gew.-% Aufbaumittel, 25 bis 50 Gew.-% oberflächenaktives System und 0 bis 25 Gew.-% Hilfsmittel enthält.
10. Mullzusammensetzung nach Anspruch 8 oder 9, dadurch gekennzeichnet, daß der Stockpunkt des oberflächenaktiven Systems weniger als 19°C (65°F) beträgt.
11. Mullzusammensetzung nach Anspruch 8 oder 9, dadurch gekennzeichnet, daß der Stockpunkt des oberflächenaktiven Systems weniger als 5°C (40°F) beträgt.
12. Mullzusammensetzung nach einem der Ansprüche 8 bis 11, dadurch gekennzeichnet, daß das oberflächenaktive System mindestens zwei nichtionogene oberflächenaktive Mittel enthält, wobei eines davon einen Stockpunkt von weniger als 5°C (40°F) aufweist.
13. Mullzusammensetzung nach einem der Ansprüche 8 bis 11, dadurch gekennzeichnet, daß das oberflächenaktive System drei nichtionogene oberflächenaktive Mittel umfaßt, von denen zwei einen Stockpunkt von weniger als 5°C (40°F) aufweisen.
14. Mullzusammensetzung nach Anspruch 8, dadurch gekennzeichnet, daß der Stockpunkt des Systems weniger als 19°C (65°F) beträgt und daß die mittlere Teilchengröße der festen Komponenten der Mullzusammensetzung 50 bis 250 µm beträgt.
15. Zuvor bemessenes, bei niedriger Temperatur wirksames Abgabesystem, dadurch gekennzeichnet, daß es einen wasserlöslichen Abgabebeutel enthält, der eine bei niedriger Temperatur wirksame Detergents-Mullzusammensetzung nach einem der vorstehenden Ansprüche einschließt.
16. Abgabesystem nach Anspruch 15, dadurch gekennzeichnet, daß der Abgabebeutel einen Film umfaßt, der aus mindestens einem gießbaren filmbildenden Polymeren, ausgewählt aus:
 Polyvinylalkohol, Polyvinylpyrrolidon, Methylcellulose, Polyethylenoxid, Gelatine und Gemischen davon, hergestellt worden ist.
17. Abgabesystem nach Anspruch 16, dadurch gekennzeichnet, daß das Polymere ein Polyvinylalkohol mit einem zahlenmittleren Molekulargewicht von 5.000 bis 250.000 und 1 bis 25% Rest-Acetatgruppen ist.

EP 0 158 464 B1

18. Abgabesystem nach einem der Ansprüche 15 bis 17, dadurch gekennzeichnet, daß der Film mindestens einen Weichmacher enthält.

19. Abgabesystem nach einem der Ansprüche 15 bis 18 dadurch gekennzeichnet, daß der Mull weiterhin (d) mindestens einen Filmweichmacher in einer Menge von nicht mehr als 30 Gew.-% des oberflächenaktiven Systems enthält.

20. Verfahren zum Waschen von Stoffen, dadurch gekennzeichnet, daß man: die Stoffe mit einer Detergens-Mullzusammensetzung nach einem der Ansprüche 1 bis 14 oder mit Waschwasser, in dem die Zusammensetzung aufgelöst oder dispergiert worden ist oder in dem ein zuvor abgemessenes, bei niedriger Temperatur wirksames Abgabesystem nach einem der Ansprüche 15 bis 19 dispergiert worden ist, kontaktiert.

Revendications

1. Une composition détergente en pâte comprenant:
 - (a) au moins un adjuvant pour détergent; et
 - (b) un système tensio-actif non ionique, et où le point d'écoulement du système est inférieur à 24°C (75°F); et la granulométrie moyenne des composants solides de la composition en pâte dépasse 10 µm; caractérisée en ce que la composition en pâte, qui ne contient pas une argile ou du dioxyde de silicium finement divisé comme agent dispersant, a un excès pondéral d'adjuvant pour détergent relativement à l'agent tensio-actif.
2. Une composition détergente en pâte efficace à basse température comprenant:
 - (a) au moins un adjuvant pour détergent; et
 - (b) un système tensio-actif non ionique, et où le point d'écoulement du système est inférieur à 24°C (75°F) et la viscosité de la composition en pâte se situe dans la gamme de 10 000 à 100 000 mPa · s; caractérisée en ce que la composition en pâte, qui ne contient pas une argile ou du dioxyde de silicium finement divisé comme agent dispersant, a un excès pondéral d'adjuvant pour détergent relativement à l'agent tension-actif.
3. Une composition selon la revendication 1 ou la revendication 2, caractérisée en ce qu'elle contient 0,1 à 5,0% en poids d'eau comme stabilisant de phase.
4. Une composition en pâte selon l'une quelconque des revendications 1 à 3, caractérisée en ce qu'au moins un adjuvant pour détergent (a) est choisi parmi:
les polyphosphates, les orthophosphates, les métaphosphates, les tripolyphosphates, les phosphates, les pyrophosphates, les carbonates, les bicarbonates, les borates, les silicates, les polysilicates, les aluminosilicates, les métaisilicates et les sels des métaux alcalins, et d'ammonium de l'un quelconque des précédents; l'acide nitrilotriacétique, les polycarboxylates, les polyhydroxysulfonates, les citrates, les succinates, les oxydisuccinates, l'acide polyacrylique, l'acide éthylènediaminetétraacétique et les sels de métaux alcalins et d'ammonium de l'un quelconque des précédents; et leurs mélanges.
5. Une composition en pâte selon l'une quelconque des revendications 1 à 4, caractérisée en ce que le système tensio-actif non ionique comprend au moins un agent tensio-actif non ionique choisi parmi:
les alcools éthoxylés linéaires et ramifiés, primaires et secondaires, ayant une longueur moyenne de la chaîne de 6 à 16 atomes de carbone et contenant, en moyenne, 2 à 10 moles d'oxyde d'éthylène par mole d'alcool; les alcools éthoxylés et propoxylés linéaires et ramifiés, primaires et secondaires, ayant une longueur moyenne de la chaîne de 6 à 16 atomes de carbone et contenant, en moyenne, 0 à 10 moles d'oxyde d'éthylène et 1 à 10 moles d'oxyde de propylène par mole d'alcool; les alcoylphénoxy (polyéthoxy)alcools linéaires et ramifiés, ayant une longueur moyenne de la chaîne de 8 à 16 atomes de carbone et contenant, en moyenne, 1,5 à 30 moles d'oxyde d'éthylène par mole d'alcool; et leurs mélanges.
6. Une composition en pâte selon l'une quelconque des revendications précédentes, caractérisée en ce qu'elle comprend de plus au moins un additif choisi parmi:
des agents tensio-actifs additionnels non ioniques, anioniques, cationiques et amphotères; des stabilisants de phase; des agents de blanchiment fluorescents; des agents d'antiredéposition; des agents inhibiteurs de la corrosion; des produits de blanchiment; des colorants; des pigments; des enzymes; des assouplisseurs de tissu; et des parfums.
7. Une composition en pâte selon la revendication 6, caractérisée en ce qu'elle comprend un agent de blanchiment fluorescent qui est au moins un des agents de blanchiment de type stilbène, styrylnaphtalène et styrène et leurs dérivés; et/ou comprenant un dit pigment qui est le bleu d'outremer; et/ou comprenant au moins une enzyme, lesquelles enzymes comprennent les amylases et les protéases.
8. Une composition en pâte selon la revendication 6 ou la revendication 7, caractérisée en ce que l'adjuvant pour détergent (a) constitue de 30% à 90% du poids, le système tensio-actif (b) constitue 10% à 70% du poids et l'additif (c) constitue 0% à 60% du poids de la composition en pâte.
9. Une composition en pâte selon l'une des revendications 6 ou 7, caractérisée en ce qu'elle comprend 50 à 75% en poids d'au moins un adjuvant pour détergent, 25 à 50% en poids de système tensio-actif et 0 à 25% en poids d'additifs.
10. Une composition en pâte selon la revendication 8 ou la revendication 9, caractérisée en ce que le point d'écoulement du système tensio-actif est inférieur à 19°C (65°F).

EP 0 158 464 B1

11. Une composition en pâte selon la revendication 8 ou la revendication 9, caractérisée en ce que le point d'écoulement du système tensio-actif est inférieur à 5°C (40°F).

12. Une composition en pâte selon l'une quelconque des revendications 8 à 11, caractérisée en ce que le système tension-actif comprend au moins deux agents tensio-actifs non ioniques dont l'une a un point d'écoulement inférieur à 5°C (40°F).

13. Une composition en pâte selon l'une quelconque des revendications 8 à 11, caractérisée en ce que le système tensio-actif comprend trois agents tensio-actifs non ioniques dont deux ont un point d'écoulement inférieur à 5°C (40°F).

14. Une composition en pâte selon la revendication 8, caractérisée en ce que le point d'écoulement du système est inférieur à 19°C (65°F) et la granulométrie moyenne des composants solides de la composition en pâte est de 50 à 250 µm.

15. Un système de distribution prédosé, efficace à basse température, comprenant: un sachet de distribution soluble dans l'eau qui renferme une composition détergente en pâte efficace à basse température selon l'une quelconque des revendications précédentes.

16. Le système de distribution de la revendication 15, dans lequel le sachet de distribution comprend une pellicule qui est préparée à partir d'au moins un polymère filmogène pouvant être coulé, choisi parmi: l'alcool polyvinylique, la polyvinylpyrrolidone, la méthylcellulose, le poly(oxyde d'éthylène), la gélatine et leurs mélanges.

17. Le système de distribution de la revendication 16, dans lequel le polymère est un alcool polyvinylique ayant une moyenne numérique du poids moléculaire de 5 000 et 250 000 et 1 à 25% de groupes acétates résiduels.

18. Le système de distribution de l'une quelconque des revendications 15 à 17, dans lequel la pellicule contient au moins un plastifiant.

19. Le système de distribution de l'une quelconque des revendications 15 à 18, dans lequel la pâte comprend de plus (d) au moins un plastifiant pour pellicule en une quantité ne dépassant pas 30% du poids du système tensio-actif.

20. Un procédé pour laver des tissus comprenant: le contact des tissus avec une composition détergente en pâte selon l'une quelconque des revendications 1 à 14 ou avec une eau de lavage dans laquelle la composition a été dissoute ou dispersée ou dans laquelle on a dispersé un système de distribution prédosé, efficace à basse température, selon l'une quelconque des revendications 15 à 19.

muffin *n.* (*English) ~, light flat round spongy cake, eaten toasted and buttered; *similar round cake made from batter or dough; ||~bell (Hist., rung by ~man, seller of muffins in street). [18th c.; orig. unkn.]

muffin *n.* small castor for sprinkling salt or sugar on muffins. [f. prec. + -ER]

muffin *n.* thick part of upper lip and nose of ruminants and rodents. [f. *F. mufte*, of unkn. orig.]

muffin *n.* receptacle in furnace where substances may be heated without contact with combustion products; similar chamber in kiln for baking painted pottery. [f. *F. mufte* mitten; cf. *MUFF*]

muffin *v.t.* wrap, cover up, (oneself, one's throat etc., or abs.) for warmth; prevent from speaking; wrap up (ears at rowlocks, bell, drum, horse's hoofs) to deaden sound for secrecy or solemnity; (usu. in *p.p.*) repress, deaden, sound of (curse etc.). [ME, perh. f. OF *emouffier* (*mouffe* thick glove, as *MUFF*)]

muffin *n.* wrap or scarf worn for warmth; thing used to deaden sound, esp. felt pad between hammer and string of piano; *silencer of motor vehicle. [f. prec. + -ER]

muffin *n.* 1. Muslim priest or expounder of law. 2. plain clothes worn by one who has right to wear uniform (esp. in *muffin*). [f. Arab. *muffit*, part. of *ʿafā* decide point of law]

mug *n.* 1. drinking-vessel, usu. cylindrical and with handle; its contents; hence ~ful 2. *n.* 2. (sl.) face, mouth; *hoodlum; ~shot, photograph of face. [prob. f. Scand.; sense 2 prob. f. grotesque faces on mugs]

mug *n.* (sl.) simpleton; gullible person; a ~'s game, senseless or unprofitable activity. [perh. f. prec. w. ref. to look of stupidity]

mug *v.* (-gg-) & *n.* (sl.) 1. *v.t.* study hard (at subject, or abs.). 2. *v.t.* ~ (up), learn (subject) by hard study. 3. *n.* one who studies hard. [19th c.; orig. unkn.]

mug *v.t.* (-gg-) thrash; strangle; rob with violence esp. in public place; hence ~ging (-g-) *n.* [prob. f. *MUG* 2]

mug *v.t.* (-gg-) (sl.) make faces, esp. before audience, camera, etc. [f. *MUG* 2]

mugger (-g-) *n.* In vbl senses. [f. *MUG* 2 + -ER]

mugger (-g-) *n.* broad-nosed Indian crocodile (*Crocodylus palustris*) venerated by many Hindus. [f. Hindi *magar*]

mugger (-g-) *n.* (pl. ~es or same). (colloq.) simpleton; person who allows himself to be outwitted; card-game like snap. [perh. the surname *M~*, w. allus. to *MUG*]

Muggletonian (-gelt-) *a.* & *n.* (member) of sect founded by, and believing in personal inspiration of, L. Muggleton and John Reeve, c. 1650. [f. Lodowick Muggleton, Engl. preacher d. 1698 + -IAN]

muggly (-gi-) *a.* (Of weather, day, etc.) oppressively damp and warm; hence ~liness *n.* [f. dial. *mug* mist, drizzle f. ON *mugga*, + -y]

Mughal Var. of *MOGUL* 1.

mugwort (-ert-) *n.* wormwood plant, esp. *Artemisia vulgaris*. [OE *mugwort* (as *MIDGE*, *WORT*)]

***mugwump** *n.* great man, boss; one who holds aloof from party politics; one who sits on the fence. [f. Algonquin *mugwump* great chief]

Muhāmmadan, Mohāmmadan, n. & a. Muslim; hence ~ism (3) *n.*, ~ize (3) *v.t.* [f. *Muhammad*, Arabian prophet d. 632 + -AN]

mulla *n.* (pl. ~s or ~es) & *a.* 1. *n.* offspring or descendant of White and Black persons. 2. *a.* of colour of mulattos, tawny. [f. Sp. *mulato* young mule, mulatto, irreg. f. *mulo* MULE]

mullberry *n.* tree of genus *Morus*, leaves of which are much used for feeding silkworms; its purple or white fruit; paper ~, small Asiatic tree (*Broussonetia papyrifera*) of same family, whose bark is used for paper-making. [ME *mol*-, *mool*-, *mulberry*, dissim. f. *murberia* f. OE **murberia*, *mārberia*, = OHG *mārberi*, *murberi* f. L. *morum*; see BERRY]

mullch (-lch, -lsh) *n.*, & *v.t.* 1. *n.* mixture of wet straw, leaves, etc., spread to protect roots of newly planted trees etc. 2. *v.t.* treat with mulch. [prob. use as *n.* of *mulch* soft; cf. dial. *melsh* mild f. OE *meluc*]

mulet *n.*, & *v.t.* (literary). 1. *n.* fine imposed for offence. 2. *v.t.* punish (person) by fine (in amount), fine (person amount); deprive (person etc. of); swindle (person), obtain by swindling. [earlier *mult(e)* f. L. *mul(c)ta*; v. thr. *F. mul(c)ter* & L. *multare*]

mule *n.* 1. offspring (usu. sterile) of he-ass and mare, or (pop.) of she-ass and stallion (prop. *hinny*), used as beast of draught and burden and undeservedly noted for obstinacy; stupid or obstinate person; hybrid plant or animal; ~canary, cross between canary and other finch. 2. kind of spinning-machine invented by Crompton, intermediate between earlier types. [ME f. OF *mul(e)* f. L. *mulus mola*]

mule *n.* Var. of MEWL.

mule *n.* backless slipper. [F]

muleteer *n.* mule-driver. [f. *F. muletier* (*mulet* dim. of OF *mul* MULE; see -ET-, -ER)]

mulla *n.* (Austral.) widely distributed shrubby acacia (*Acacia aneura*); its wood; scrub, bush; (colloq.) outback. [Aboriginal]

mullibrity *n.* womanhood; normal characteristics of a woman (opp. *virility*); softness, effeminacy. [f. LL *muliebritas* f. L. *mulier* woman; see -ITY]

mullish *a.* like a mule; stubborn; hence ~ly *adv.*, ~ness *n.* [f. MULE + -ISH]

mull *n.* thin soft plain muslin. [abbr. of *mulmull* f. Hindi *malma*]

mull *n.* & *v.* (colloq.) 1. *n.* ||muddle, mess, (make a mull of). 2. *v.t.* ||make a mull of (catch at cricket etc.). 3. *v.t.* & *i.* ponder (over). [perh. f. *mull* grind to powder, ME *mul* dust f. MDu.]

mull *v.t.* make (wine, beer) into hot drink with sugar, spices, egg-yolk, etc. [17th c.; orig. unkn.]

mull *n.* (Sc.) promontory (*Mull of Kintyre*). [ME; cf. Gael. *maol*, Icel. *mull*]

mull *n.* (Sc.) snuff-box. [var. of MULL, box orig. having a grinder]

mull *n.* humus formed under non-acid conditions. [G. f. Da. *muld*]

mullak (-a) *n.* Muslim learned in Islamic theology and sacred law. [f. Pers., Turk., Urdu *mulla* f. Arab. *maula*]

mullein (-lin) *n.* herbaceous plant of genus *Verbascum*, with woolly leaves and yellow flowers. [ME, f. OF *moleine* f. Gaulish **melena*]

muller *n.* stone etc. used for grinding powders etc. on slab. [ME, perh. f. AF **moloir* (*moldre* grind; see -ER)]

mullet *n.* fish of family Mullidae (red ~) or Mugilidae (grey ~), valued for food. [ME, f. OF *mulet* dim. f. L. *mullus* red mullet f. Gk *mollus*]

***mulligan** *n.* (colloq.) stew of odds and ends of food; [perh. f. name *Mulligan*]

mulligatawny *n.* highly seasoned soup orig. from India; ~paste, curry paste used for this. [f. Tamil *muligatawny* pepper-water]

mulligrubs (-z) *n.* pl. depression of spirits; stomach-ache. [16th c. *multigrubs*, of unkn. orig.]

mullion (-yon) *n.* vertical bar dividing lights in window (cf. *TRANSOM*); hence ~ed (-yond) *a.* [prob. metathetic f. *MOMIAL*]

mulluck *n.* 1. (Austral. & dial.) refuse, rubbish. 2. (Austral.) rock containing no gold; refuse from which gold has been extracted; ridicule. [ME dim. of *mul* dust, rubbish, f. MDu.; see -OCK]

mulloway (-owā) *n.* (Austral.) large marine food-fish (*Sciaen antarctica*). [19th c.; orig. unkn.]

mulltangular (-ngg-) *a.* many-angled. [f. med. L. *multangularis* (as *MULTI*-, *ANGULAR*)]

multurety *n.* (arch.) manifoldness. [f. L. *multus* many; cf. *HAECCEITY*]

multurety *pref.* many; as: ~colour(ed), of many colours; ~fid, (Bot. & Zool.) cleft into many parts; ~foil, (Archit.) ornament consisting of more than 5 foils;

multifarious *~form*, hav-
~for'mity *n.*
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languages; ~
several millio-
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